

## The Mechanism of Hydrated Proton Transport in Water

Tyler J. F. Day, Udo W. Schmitt, and Gregory A. Voth\*

Department of Chemistry and  
Henry Eyring Center for Theoretical Chemistry  
315 South 1400 East, RM 2020, University of Utah  
Salt Lake City, Utah 84112-0850

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Proton transport (PT) is a process of fundamental importance to the fields of chemistry, physics, and biochemistry. Protons in liquid water exhibit mobilities which are considerably greater than those of other simple monovalent cations. This anomalously high diffusion rate is most often attributed to the Grötthaus mechanism, by which the hydronium species ( $H_3O^+$ ) is able to shuttle a proton to a water molecule in its first solvation shell, which can then in turn shuttle to yet another molecule. By transporting via this mechanism, an excess proton is able to diffuse throughout the entire hydrogen bond network of water at a rate considerably greater than that of conventional diffusion. The mechanism, as well as the rate-limiting step, of this process is a topic of considerable interest.

It has been shown elsewhere<sup>1–4</sup> that the solvation state of the hydronium species in aqueous systems is considerably different from that of a simple water molecule. In particular, the coordination number of hydronium observed in molecular dynamics simulations is typically 3.0, as compared to 3.9 for bulk water.<sup>1–4</sup> Consequently, as the proton is transferred to a recipient water molecule, a significant rearrangement of the local hydrogen bond network must occur. Namely, one would expect to observe hydrogen bond cleavage on the recipient oxygen site, as well as subsequent hydrogen bond formation on the donor oxygen. It has been speculated<sup>5,6</sup> that the actual rate-limiting step of the PT mechanism involves this breaking of hydrogen bonds in the second solvation shell of the hydronium, which then allows the proton transfer to occur. This transfer is then immediately followed by hydrogen bond formation on the donor oxygen. Agmon,<sup>5</sup> and later Vuilleumier and Borgis,<sup>4</sup> referred to this as the “Moses mechanism” due to the analogy of Moses parting the Red Sea. Some evidence of this mechanism has indeed been found,<sup>4</sup> although the results were not conclusive. It is the goal of the current work to shed further light on the PT mechanism.

The treatment of an excess proton in aqueous solution requires a quantitatively accurate potential energy surface (PES) for the PT process. While the various well-established electronic structure methods are able to generate this surface with reasonable accuracy, these methods are numerically demanding and thus not always of practical use when studying condensed-phase systems over long time scales. However, the Empirical Valence Bond (EVB) methodology, originally pioneered by Coulson<sup>7</sup> and Mulliken<sup>8</sup> and further developed by Warshel,<sup>9,10</sup> has been successfully employed in the study of chemical reactions. This methodology

allows for the accurate construction of the PES for species undergoing reaction in a manner that is numerically very efficient, even for many-body systems, and is thus ideal for use in molecular dynamics (MD) simulations. While there have been several EVB models developed for the treatment of an excess proton in water,<sup>2,11–16</sup> the one employed in the current work is an extension of our previous two-state model to a generalized multi-state one, called the MS-EVB model.<sup>2</sup> This model reproduces the experimental PT rate and agrees well with the equilibrium results from much more demanding and complementary first-principle MD simulations.<sup>17</sup>

To conduct a thorough investigation of the PT mechanism, a very large number of transfer events are required. While the most obvious method for generating this ensemble of reactive paths is through straightforward time propagation of the system, this is not always of practical use. In many systems, the event being studied occurs on a time scale that makes the generation of such a large ensemble prohibitively expensive. Recently, however, a technique to reliably and efficiently generate such an ensemble has been developed.<sup>18,19</sup> The transition path sampling method allows for the generation of a large number of properly weighted reactive trajectories in a numerically efficient manner, and was used to generate the proton-transfer trajectories in the current work.

As discussed above, the dynamical process of interest is the transfer of an excess proton along the hydrogen bond network of bulk phase water. Consequently, the reaction is the transfer of a proton from the hydronium species to one of the first shell waters. However, this raises certain practical problems. In particular, it proves difficult to distinguish between an actual transfer (in which case the recipient oxygen forms a stable hydronium product) from small fluctuations in the EVB amplitudes, which do not constitute a successful transfer event. In an effort to eliminate the contribution from these oscillations, the actual reactive process investigated was the transfer of a proton between two oxygen sites ( $O_i$  and  $O_j$ ) via an intermediate ( $O_2$ ), similar to the approach used by Vuilleumier and Borgis.<sup>4</sup> This removes the possibility of such fluctuations and guarantees that the reactive trajectories generated involve actual proton-transfer events. A total of 400 reactive trajectories were generated using the techniques discussed above, employing a single excess proton and 125 water molecules under periodic boundary conditions, as in ref 2.

To examine the proton-transfer mechanism, the instant in time at which the actual transfer occurs must be identified. For the purposes of this work, the *protonation time* will be defined as the *first* instance in which  $O_3$  represents the dominant EVB state. Similarly, the *deprotonation time* will be defined as the *last* instance in which  $O_1$  represents the dominant EVB state. It should be noted that, since the proton transfer occurs via an intermediate ( $O_2$ ), these two times are not the same. Using these two definitions, it is possible to study the protonation and deprotonation events independently.

The number of hydrogen bonds present for both  $O_1$  and  $O_3$  as a function of time is depicted in Figure 1. For our purposes, we have used Vuilleumier and Borgis' definition of a hydrogen bond:<sup>4</sup>  $R_{OO} \leq 3.60 \text{ \AA}$ ,  $R_{OH} \leq 2.45 \text{ \AA}$ , and  $\phi_{OHO} \leq 45^\circ$ , where  $R_{OO}$  is the

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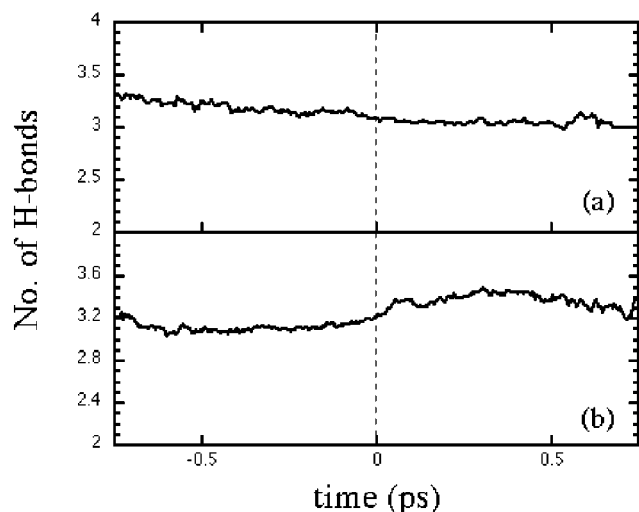
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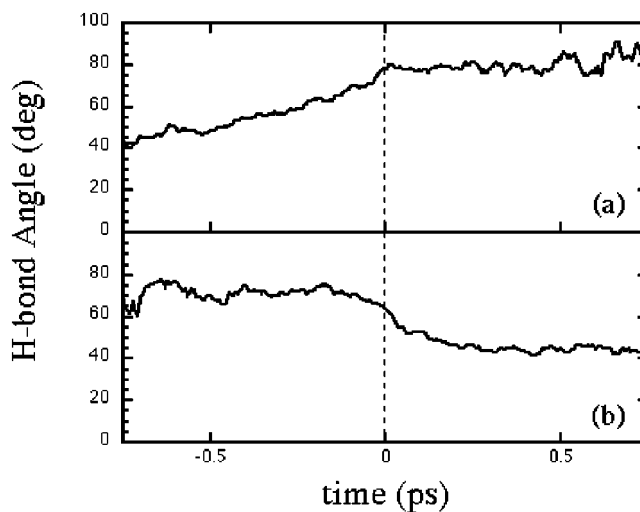


**Figure 1.** Average number of H-bonds as a function of time for (a)  $O_3$  and (b)  $O_1$ . The time origins ( $t = 0$ ) correspond to (a) the protonation time and (b) the deprotonation time.

oxygen–oxygen distance,  $R_{OH}$  is the oxygen–hydrogen distance, and  $\phi_{HO}$  is the hydrogen bond angle. Though a slight decrease in the number of hydrogen bonds for  $O_3$  upon protonation, as well as a corresponding increase in number for  $O_1$ , is evident, the effect is not very pronounced. This is in agreement with previous findings,<sup>4</sup> and is most likely a result of the insensitivity of this particular quantity to the proton-transfer mechanism. While the PT does indeed appear to involve restructuring of the local hydrogen bond network, a quantity that is more sensitive to the mechanism is required. For example, instead of selecting a maximum value for the hydrogen bond angle and examining the number of hydrogen bonds satisfying this condition, examining the time-evolution of the hydrogen bond angles themselves proves to be considerably more useful.

On average, a water molecule in the bulk phase has a coordination number of approximately 3.9, and thus possesses 4 potential hydrogen bonds, 2 of which it donates to first shell water molecules, and 2 of which it accepts from them. During a proton-transfer event, one of these two “acceptor” hydrogen bonds must, in fact, correspond to the proton-transfer coordinate. Upon receiving the excess proton, this acceptor bond becomes a donor bond, leaving the newly formed hydronium with 3 donor hydrogen bonds, one for each of its protons. It is the fate of the remaining acceptor bond that is of primary interest. To examine the state of this hydrogen bond as the PT occurs, the hydrogen bond angle for this acceptor bond was determined at each point in time by first locating all water molecules within a distance of 3.6 Å of the oxygen of interest. From these first shell waters, the best acceptor hydrogen bond, excluding the proton-transfer coordinate itself, was determined and the bond angle calculated.

The results for both the reactant ( $O_1$ ) and product ( $O_3$ ) oxygens are shown in Figure 2. In contrast to the results presented in Figure 1, the results in Figure 2 show a very pronounced effect from the proton transfer. The acceptor hydrogen bond on  $O_3$  (Figure 2a) shows distinct signs of cleavage in connection with the acceptance of the excess proton. Similarly, hydrogen bond formation is clearly evident in connection with the deprotonation



**Figure 2.** Average H-bond angle of the best acceptor bond as a function of time for (a)  $O_3$  and (b)  $O_1$ , excluding the proton-transfer coordinate.

of  $O_1$  (Figure 2b). Interestingly, the hydrogen bond cleavage on  $O_3$  occurs prior to the actual PT event itself, suggesting that it is indeed the breaking of this bond that is the rate-limiting step in the overall mechanism.<sup>2</sup> In contrast, the hydrogen bond formation on  $O_1$  occurs following the transfer, and thus does not appear to play as important a role in the transfer. This is in very clear agreement with the proposed Moses mechanism.<sup>5</sup>

The dependence of the proton transfer on this hydrogen bond cleavage suggests that these bonds interfere to some degree with the hydronium–water interaction. Ab initio calculations<sup>20</sup> indicate that the ground state form of the protonated water dimer is, in fact, the symmetric Zundel ( $H_5O_2^+$ ) species. In contrast, bulk phase simulations<sup>2,3,17</sup> indicate that both the Zundel and Eigen ( $H_3O^+$ ) species play important roles. This suggests that the presence of the extended hydrogen bond network in the condensed phase interferes somewhat with the interaction between the hydronium and its first shell waters. Only upon breaking of this extended hydrogen bond network does the Zundel species form, facilitating the proton transfer. The extended hydrogen bond network is quite dynamic in nature, however, with a bond lifetime on the order of a few picoseconds, and hence a PT rate on the same time scale.

In summary, we have found statistically clear evidence of the proposed Moses mechanism for proton transport in liquid water. Hydrogen bond cleavage in the second solvation shell allows for the exchange of a proton between the hydronium and a neighboring water molecule. Only following this transfer is hydrogen bond formation observed on the proton donor oxygen, as it returns to a more water-like environment.

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